

catalysts in polymer production depends on the cost and efficiency of the system. Metallocene catalysts cost significantly more than the traditional Ziegler-Natta catalysts but the metallocene systems are considerably more productive. In some cases, the increased productivity of metallocene catalysts relative to the Ziegler-Natta catalysts ranges from one to two orders of magnitude more polymer produced per pound of catalyst.

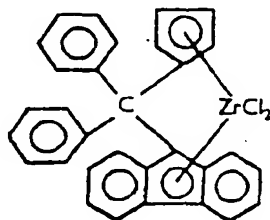
Since the recent introduction of aluminoxane-activated metallocene catalysts for the production of polyethylene, polypropylene, and copolymers of ethylene and α -olefins such as linear low density polyethylene (LLDPE), some effort has been made to apply these catalysts to the production of EPDM elastomers. For this use, it is desired that the catalyst produce high yields of EPDM in a reasonable polymerization time, result in adequate incorporation of the diene monomer(s) and provide a random distribution of monomers while enabling good control of M_w over a wide range while yielding a relatively narrow MWD.

Kaminsky et al., J. Poly. Sc., Vol. 23, 2151-2164 (1985), discloses the use of a metallocene-methylaluminoxane (MAO) catalyst system to produce low molecular weight EPDM elastomers, i.e., M_w s of not greater than about 150,000. Such catalysts require long reaction times and provide low yields and are therefore impractical for commercial EPDM manufacture. Similarly, Japanese Patent 62-121,771 describes a metallocene-catalyzed polymerization process yielding an ethylene-1-butene-diene elastomer of high ethylene content in low yield.

Other polymerization processes for producing EPDMs featuring the use of a metallocene catalyst activated by an

aluminoxane such as MAO are described, e.g., in U.S. Patent Nos. 4,871,705, 5,001,205, 5,229,478 and 5,442,020, EP 347,129 and WO 95/16716. As discussed more fully below, the lack of more widespread commercial implementation of metallocene catalysts where the production of high molecular weight elastomers is concerned is due at least in part to the need to use very large amounts of aluminoxane cocatalyst to activate the metallocene to acceptable levels.

EPA 593,083 describes a gas phase polymerization process for producing EPDM employing a bridged metallocene catalyst (1):

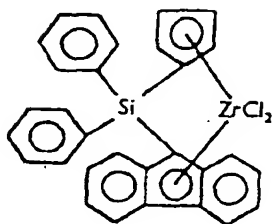


1
diphenylmethylene
(cyclopentadienyl)(fluorenyl)
zirconium dichloride

Gas phase polymerization, however, is prone to a number of technical difficulties, reactor fouling among them, that need to be overcome before this type of process for producing EPDM elastomers will achieve general acceptance by the industry.

EPA 612,769 and EP 653,445 both disclose the use of metallocene catalyst (1) in a solution phase polymerization process for producing linear low [molecular weight] propylene-diene elastomer (LLPDE) in contrast to a high molecular weight elastomer that is an object of the present invention.

U.S. Patent No. 5,401,817 describes a polymerization process employing bridged metallocene catalyst (2):

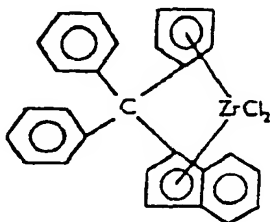


2

diphenylsilyl(cyclopentadienyl)
(fluorenyl)zirconium dichloride

There is, however, no mention of producing an elastomer in this patent.

Green et al., J. Chem. Soc. Dalton Trans., 657-665 (1994) describes the polymerization of propylene and styrene employing a bridged metallocene catalyst (3):



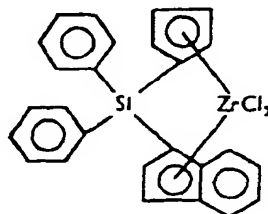
3

diphenylmethylene
(cyclopentadienyl)(indenyl)
zirconium chloride

No mention of producing an elastomer is made in this publication.

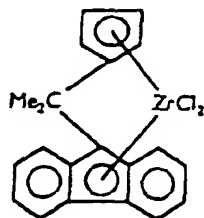
Kaminsky et al., Angew. Chem. Int. Ed. Engl., 34, 2273-2275 (1995) describes bridged metallocene catalyst (4),

together with MAO, for the copolymerization of ethylene with bulky cycloalkenes:



4
diphenylsilyl
(cyclopentadienyl)(indenyl)
zirconium dichloride

Another aspect of the present invention lies in the discovery that not all bridged metallocene catalysts will provide high molecular weight elastomers. Thus, e.g., it has been found that bridged metallocene catalyst (5)

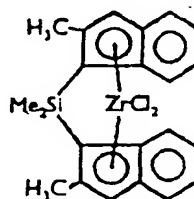


5
dimethylmethylenecyclopentadienyl
(cyclopentadienyl)(fluorenyl)
zirconium dichloride

which differs from metallocenes (1)-(4), supra, only in the nature of the bridging group joining the two cyclopentadienyl-derived ligands provides low molecular weight (<50,000) ethylene-propylene copolymers. In contrast to this result and as discovered herein, activated

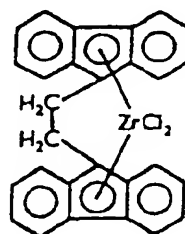
metallocene catalyst (1) provides elastomers of high molecular weight (>300,000).

Bridged metallocene catalysts (6) and (7) possessing the bis(indenyl) and the bis(fluorenyl) structures, respectively, are capable of providing high molecular weight amorphous ethylene-propylene copolymers:



6

racemic-dimethylsilyl
bis(2-methylindenyl)
zirconium dichloride



7

ethylene-bridged
bis(fluorenyl)
zirconium dichloride

Metallocenes (6) and (7) are described in U.S. Patent Nos. 5,145,819 (indenyl) and 5,436,305 (fluorenyl) for the production of homopolymers. No mention is made in either patent of employing the disclosed metallocene for the production of an EPDM-type elastomer.

As previously mentioned, it has been discovered that one of the obstacles to widespread commercial

implementation of metallocene catalysis lies in the use of an aluminoxane as cocatalyst. Aluminoxanes are expensive and large amounts are required in order to activate the metallocene catalyst with which they are associated.

5

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a liquid phase polymerization process, i.e., one carried out under solution or slurry conditions and in batch or continuously, for producing a polyolefin elastomer employing as the catalyst composition an activated bridged metallocene in which the bridging group possesses at least two bulky groups.

It is a further object of the invention to provide such a process for the polymerization of olefins to provide high molecular weight EP and EODEs such as the EPDMs.

Yet another object of the invention is to provide a catalytically active composition comprising a metallocene procatalyst activated by a particular type of cation-generating cocatalyst.

Additional objects of the invention include providing a polyolefin elastomer possessing a combination of high molecular weight, high Mooney viscosity, low polydispersity index, low glass transition temperature and low hysteresis and various products manufactured therefrom.

In keeping with these and other objects of the invention, there is provided a process for the liquid phase polymerization of ethylene, at least one other α -olefin and, optionally, at least one diene monomer to provide an elastomer, the process comprising contacting the monomer under liquid phase polymerization conditions with a catalytically effective amount of a catalyst composition comprising the product obtained by combining (a) a metallocene procatalyst, preferably one containing a

bridging group possessing at least two bulky groups, and (b) a cocatalyst, preferably a cation-generating cocatalyst as hereinafter described.

The polyolefin elastomers obtained by the process of this invention are themselves novel, possessing, in combination, a higher molecular weight (M_w), higher Mooney viscosity (ML_{1+4} at 125°C) a lower polydispersity index (M_w/M_n), a lower glass transition temperature (T_g) and a lower hysteresis ($\tan \delta$) than these same properties in known polyolefin elastomers incorporating equivalent amounts of the same olefins. These elastomers confer advantageous properties on products manufactured therefrom relative to the same products manufactured from known elastomers.

The terms "metallocene" and "metallocene procatalyst" as used herein shall be understood to refer to compounds possessing a transition metal M, at least one non-cyclopentadienyl-derived ligand X and zero or one heteroatom-containing ligand Y, the ligands being coordinated to M and corresponding in number to the valence thereof. Such compounds, cocatalysts useful for their activation to provide metallocene catalysts that may be employed for the polymerization of olefins to provide polyolefin homopolymers and copolymers and/or polymerization processes employing one or more of the metallocene catalysts are described in, among others, U.S. Patent Nos. 4,752,597; 4,892,851; 4,931,417; 4,931,517; 4,933,403; 5,001,205; 5,017,714; 5,026,798; 5,034,549; 5,036,034; 5,055,438; 5,064,802; 5,086,134; 5,087,677; 5,126,301; 5,126,303; 5,132,262; 5,132,380; 5,132,381; 5,145,819; 5,153,157; 5,155,080; 5,225,501; 5,227,478; 5,229,478; 5,241,025; 5,243,002; 5,278,119; 5,278,265; 5,281,679; 5,296,434; 5,304,614; 5,308,817; 5,324,800; 5,328,969; 5,329,031; 5,330,948; 5,331,057; 5,349,032; 5,372,980; 5,374,753; 5,385,877; 5,391,629; 5,391,789; 5,399,636; 5,401,817;

5,406,013; 5,416,177; 5,416,178; 5,416,228; 5,427,991;
 5,439,994; 5,441,920; 5,442,020; 5,449,651; 5,453,410;
 5,455,365; 5,455,366; 5,459,117; 5,466,649; 5,470,811;
 5,470,927; 5,477,895; 5,491,205; and, 5,491,207, the
 5 contents of which are incorporated by reference herein.

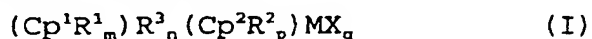
BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graphical comparison of the stability of a metallocene procatalyst activated by cation-generating cocatalysts both within (Example 21) and outside (Comparative Example 30) the scope of the invention, the stability of the catalysts being shown as the amount of monomer consumed over time.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymerization process herein employs a catalyst composition obtained by activating a metallocene procatalyst with a suitable cocatalyst.

The metallocene procatalyst is preferably one or a mixture of metallocene compounds of either or both of the following general formulae:

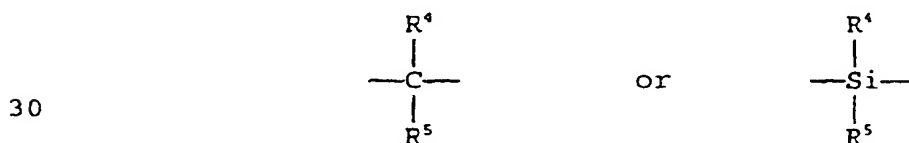


wherein Cp^1 of ligand $(\text{Cp}^1\text{R}^1_m)$ and Cp^2 of ligand $(\text{Cp}^2\text{R}^2_p)$ are the same or different cyclopentadienyl rings, R^1 and R^2 each is, independently, halogen or a hydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, m is 0 to 5, p is 0 to 5 and two R^1 and/or R^2 substituents on adjacent carbon atoms of the cyclopentadienyl ring associated therewith can be joined together to form a ring containing from 4 to about 20 carbon atoms, R^3 is a bridging group, n is 0 or 1, Y is a heteroatom-containing ligand in which the heteroatom is

coordinated to M, M is a transition metal having a valence of from 3 to 6, each X is a non-cyclopentadienyl ligand and is, independently, halogen or a hydrocarbyl, oxyhydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid, oxyhydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, q is equal to the valence of M minus 2, r has the value of n and s is equal to the valence of M minus 1 when r is 0 and is equal to the valence of M minus 2 when r is 1.

Methods for preparing these and other useful metallocene procatalysts are known in the art and do not constitute a part of the present invention.

Metallocene procatalyst (I) can be activated either with an aluminoxane or, preferably, with the cation-generating cocatalyst hereinafter described. If the metallocene procatalyst is entirely one of formula (II), it is activated with the aforementioned cation-generating cocatalyst. However, where the metallocene procatalyst is one of formula (I) and the cocatalyst is entirely an aluminoxane, ligand (Cp^1R^1_m) must be different from ligand (Cp^2R^2_p), bridging group R^3 must contain at least two bulky groups and the value of n must be 1. Of these bridged metallocenes, it is preferred that bridging group R^3 possess the structure



in which bulky groups R^4 and R^5 each, independently, is, or contains, a cyclohydrocarbyl group containing up to about 20, and preferably from 6 to about 12, carbon atoms and from 0 to 3 heteroatoms such as oxygen, sulfur, tertiary

nitrogen, boron or phosphorus and, in particular, is a cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, heteroaryl, alkaryl, alkylheteroaryl, aralkyl, heteroaralkyl, and so forth, M is titanium, zirconium or hafnium, q is 2 and each X is halogen.

Of this preferred group of bridged metallocenes, those in which ligand (Cp^1R_m^1) is unsubstituted cyclopentadienyl, ligand (Cp^2R_p^2) is indenyl or fluorenyl, M is zirconium, R^4 and R^5 each is phenyl and each X ligand is chlorine are still more preferred. These more preferred metallocenes correspond to known metallocene compounds (1)-(4), supra.

Still other preferred bridged metallocenes (I) that can be used in the polymerization process of this invention include:

diphenylmethylen(indenyl)(fluorenyl)zirconium dichloride,
diphenylmethylen(cyclopentadienyl)(4,5,6,7-tetrahydroindenyl)zirconium dichloride,
diphenylmethylen(cyclopentadienyl)(2-methylindenyl)zirconium dichloride,
diphenylmethylen(2,4-dimethylcyclopentadienyl)(3',5'-dimethylcyclopentadienyl)zirconium dichloride,
diphenylmethylen(2-methyl-4-tert-butylcyclopentadienyl)(3'-tert-butyl-5'-methylcyclopentadienyl)zirconium dichloride,
dixylylmethylen(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)zirconium dichloride,
dixylylmethylen(2,4-dimethylcyclopentadienyl)(3',5'-dimethylcyclopentadienyl)zirconium dichloride,
dixylylmethylen(2-methyl-4-tert-butylcyclopentadienyl)(3'-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride,
dixylylmethylen(cyclopentadienyl)(fluorenyl)zirconium dichloride,

- di-o-tolylmethylenecyclopentadienyl (3,4-dimethylcyclopentadienyl)zirconium dichloride,
di-o-tolylmethylenecyclopentadienyl (3,4-dimethylcyclopentadienyl)zirconium dichloride,
5 di-o-tolylmethylenecyclopentadienyl (3,4-dimethylcyclopentadienyl)zirconium dichloride,
di-o-tolylmethylenecyclopentadienyl (indenyl)zirconium dichloride,
dibenzylmethylenecyclopentadienyl (tetramethylcyclopentadienyl)zirconium dichloride,
10 dibenzylmethylenecyclopentadienyl (indenyl)zirconium dichloride,
dibenzylmethylenecyclopentadienyl (fluorenyl)zirconium dichloride,
15 dicyclohexylmethylenecyclopentadienyl (indenyl)zirconium dichloride,
dicyclohexylcyclopentadienyl (fluorenyl)zirconium dichloride,
dicyclohexylmethylenecyclopentadienyl (fluorenyl)zirconium dichloride,
20 diphenylsilyl (2,4-dimethylcyclopentadienyl) (3',5'-dimethylcyclopentadienyl)zirconium dichloride,
diphenylsilyl (2,4-dimethylcyclopentadienyl) (3',5'-dimethylcyclopentadienyl)zirconium dichloride,
25 diphenylsilyl (2,3,5-trimethylcyclopentadienyl) (2,4,5-trimethylcyclopentadienyl)zirconium dichloride,
tetraphenyldisilyl (cyclopentadienyl) (indenyl)zirconium dichloride,
tetraphenyldisilyl (3-methylcyclopentadienyl) (indenyl)zirconium dichloride,
30 tetraphenyldisilyl (cyclopentadienyl) (fluorenyl)zirconium dichloride,
di-o-tolylsilyl (cyclopentadienyl) (trimethylcyclopentadienyl)zirconium dichloride,

di-o-tolylsilyl(cyclopentadienyl)(tetramethylcyclopenta-
dienyl)zirconium dichloride,
di-o-tolylsilyl(cyclopentadienyl)(3,4-diethylcyclopenta-
dienyl)zirconium dichloride,
5 di-o-tolylsilyl(cyclopentadienyl)(triethylcyclopentadienyl)
zirconium dichloride,
dibenzylsilyl(cyclopentadienyl)(fluorenyl)zirconium
dichloride,
dibenzylsilyl(cyclopentadienyl)(2,7-di-t-butyl-
10 fluorenyl)zirconium dichloride, and
dicyclohexylsilyl(cyclopentadienyl)(fluorenyl)zirconium
dichloride.

In the preferred metallocene procatalysts of
formula (II), n and r are both 1, the valence of M is 4, X
15 is halogen and s is 2. Illustrative of such preferred
metallocene procatalysts (II) that can be activated by the
cation-generating cocatalyst of this invention are the
following:
dimethylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)
20 zirconium dichloride,
dimethylsilyl(3,4-dimethyl cyclopentadienyl)(cyclohexyl-
amido)hafnium dichloride,
dimethylsilyl(tetramethylcyclopentadienyl)(butylamido)
titanium dichloride,
25 dimethylsilyl(3,4-di-t-butylcyclopentadienyl)(cyclododecyl-
amido)titanium dichloride,
dimethylsilyl(2,5-dimethylcyclopentadienyl)(cyclododecyl-
amido)titanium dichloride,
di-n-propylsilyl(2,5-dimethylcyclopentadienyl)(p-n-butyl-
30 phenylamido)titanium dichloride,
di-isopropylsilyl(2-indenyl)(cyclohexylamido)zirconium
dihalide,
diphenylsilyl(tetra-n-propylcyclopentadienyl)(isopropyl-
amido)zirconium dihalide, and

dimethylmethylene(2-methyl-5-t-butylcyclopentadienyl)
(dimethylamido)zirconium dihalide.

The cocatalyst, or activator, employed with the preferred bridged metallocene procatalysts of formula (I) can, as previously stated, be any of the aluminoxanes known to activate metallocene procatalysts. For further details of the aluminoxane cocatalysts including such alkylaluminoxanes as MAO see, e.g., U.S. Patent No. 5,227,478. In general, the bridged metallocene procatalyst can be present in the reactor in an amount, expressed in terms of its transition metal content, of from about 0.0001 to about 0.02, preferably from about 0.0002 to about 0.015 and more preferably from about 0.0002 to about 0.01, millimoles/liter. Corresponding to these amounts of transition metal, the aluminoxane cocatalyst can be utilized in an amount of from about 0.01 to about 100, preferably from about 0.02 to about 75 and more preferably from about 0.025 to about 50, millimoles/liter. It will, of course, be recognized that optimum levels of bridged metallocene procatalyst and aluminoxane cocatalyst will to some extent depend upon the specific procatalyst and cocatalyst selected as well as other polymerization process variables.

When employing an aluminoxane cocatalyst, it can be advantageous to include a trialkylaluminum such as trimethylaluminum, triethylaluminum, tri(n-propyl)aluminum, triisopropylaluminum, tri(n-butyl)aluminum, triisobutylaluminum, and the like, to reduce the amount of aluminoxane required for suitable activation of the metallocene procatalyst. In general, the optional trialkylaluminum can be utilized in a molar ratio to metallocene procatalyst of from about 1 to about 1000 and preferably from about 2 to about 500.

Preferably, however, the cation-generating cocatalyst of the composition described below is used to activate metallocene procatalysts (I) and (II). This preferred cocatalyst can be used as a partial or complete replacement for the aluminoxanes, not only for the preferred bridged metallocenes described above, but for any of the metallocene procatalysts, whether bridged or nonbridged, with which the invention is concerned. More particularly, the cation-generating cocatalyst herein comprises: as a first component, a metal- and/or metalloid-containing compound capable of exchanging at least one X ligand in the metallocene procatalyst up to the total number thereof with, independently, a hydrogen atom or a carbohydryl group containing up to about 20 carbon atoms or oxycarbohydryl group containing up to 20 carbon atoms; as a second component, a neutral metal- and/or metalloid-containing compound having at least one aryl group possessing at least one electron-withdrawing substituent; and, as a third component an anionic metal- and/or metalloid-containing compound having at least one aryl group possessing at least one electron-withdrawing substituent.

Activation of the metallocene procatalyst can be achieved by combining the metallocene with the aforementioned components of the cation-generating cocatalyst either simultaneously or in any sequence and with any interval of time therebetween. For reasons discussed below, in situ activation of the procatalyst, i.e., within the polymerization reactor in the presence of monomer, is preferred. However, it is also within the scope of the invention to achieve activation of the procatalyst in other ways, for example, by reacting the metallocene procatalyst with the first component of the cocatalyst and thereafter combining the product of this reaction with the second and third components of the cocatalyst either simultaneously or

sequentially either within, or in the absence of, the olefin monomer. In general, the molar ratio of the first component of the cocatalyst to metallocene procatalyst can vary from 1 to about 500 and preferably from about 2 to about 500 and
5 the molar ratios of the second and third components of the cocatalyst to metallocene procatalyst can, independently, vary from about 0.5 to about 10 and preferably from about 0.8 to about 5.

The metal- or metalloid-containing first component
10 for providing the cation-generating cocatalyst herein can advantageously be an aluminum compound of the general formula $AlR^4R^5R^6$ in which R^4 , R^5 and R^6 each, independently, is a hydrocarbyl, e.g., alkyl, or oxyhydrocarbyl, e.g., alkoxy, group containing up to about 20 carbon atoms, or
15 hydrogen, provided that no more than two of R^4 , R^5 and R^6 can be hydrogen. Suitable aluminum compounds include trimethylaluminum, triethylaluminum, tri(n-propyl)aluminum, triisopropylaluminum, tri(n-butyl)aluminum, tri(n-propyl)aluminum, triisobutylaluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum, dimethylaluminum hydride, diethylaluminum
20 hydride, diisopropylaluminum hydride, di(n-propyl)aluminum hydride, diisobutylaluminum hydride, di(n-butyl)aluminum hydride, dimethylaluminum ethoxide, di(n-propyl)aluminum ethoxide, diisobutylaluminum ethoxide, di(n-butyl)aluminum
25 ethoxide, and the like. Of the foregoing aluminum compounds, the trialkylaluminums are preferred and of these, triethylaluminum and triisobutylaluminum are more preferred. Additional representatives of compounds that can be used as the first component of the cocatalyst are alkali metal
30 organometallics, alkaline earth organometallics and organometal halides (e.g., Grignard reagents), hydrocarbyl complexes of such metals and organometalloids such as those of boron, zinc, gallium, germanium, arsenic, tellurium mercury, lead, and the like.

Useful second components for providing the preferred cocatalysts include boranes such as tris(pentafluorophenyl)borane, tris(methoxyphenyl)borane, tris(trifluoromethyl-phenyl)borane, tris(3,5-di(trifluoromethyl)phenyl)borane, tris(tetrafluoroxyl)borane, tris(tetrafluoro-o-tolyl)borane, and the like. Of the foregoing boranes, tris(pentafluorophenyl)borane and tris(3,5-di(trifluoromethyl)phenyl)borane are preferred. Other useful second components include aluminum homologues of the foregoing compounds.

Specific third components that can be used in the preferred cocatalysts include borates such as lithium tetrakis(pentafluorophenyl)borate, lithium tetrakis(trifluoromethylphenyl)borate, lithium tetrakis(3,5-di(trifluoromethyl)phenyl)borate, sodium tetrakis(pentafluorophenyl)borate, potassium tetrakis(pentafluorophenyl)borate, magnesium tetrakis(pentafluorophenyl)borate, titanium tetrakis(pentafluorophenyl)borate, tin tetrakis(pentafluorophenyl)borate, and the like. Of the foregoing borates, alkali metal borates such as lithium tetrakis(pentafluorophenyl) borate and lithium tetrakis(3,5-di(trifluoromethyl)phenyl)borate are preferred. Other useful third components include aluminate homologues of the foregoing compounds.

The activated metallocene catalyst composition can be prepared in advance and thereafter introduced into the polymerization reactor. However, when employing the preferred cation-generating cocatalyst, supra, it is highly preferred to activate the metallocene procatalyst with the cocatalyst components in situ, which is to say, in the presence of monomer. There are considerable advantages to such in situ activation.

The metallocene procatalysts in which each X ligand is a halogen are fairly stable compounds and impose

no special handling or storage requirements. However, the metallocenes in which one or more X ligands is a hydrogen atom or a hydrocarbyl group are highly susceptible to degradation when exposed to oxygen, moisture, light and/or heat. When prepared in advance, care must be taken to store these metallocenes in a manner which will exclude all of these conditions. This is especially the case with the metallocene hydrides which are extremely unstable. For these reasons, it is preferred to activate the metallocene procatalyst with the preferred cocatalyst within the polymerization reactor in the presence of monomer. Activating the procatalyst in this way avoids or greatly diminishes the possibility of forming catalytically inactive degradation products.

There are still other significant advantages to in situ activation of the metallocene procatalyst. Thus, in situ activation offers the flexibility of adjusting the quantity of aluminum component in the cocatalyst to compensate for process conditions in the polymerization reactor, e.g., via reactive scavenging of polar impurities. Use of preformed metallocene hydrides, hydrocarbyls or oxyhydrocarbyls would necessitate an independent feed of such a scavenger such representing a complication of the polymerization process. In addition, it has been observed herein that activation in the presence of olefin monomer results in significantly higher initial polymerization activity than the same catalyst activated in advance of its introduction into the polymerization reactor.

The α -olefins suitable for use in the preparation of the elastomers herein contain from 3 to about 20 carbon atoms and include propylene, 1-butene, 3-methylbutene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, and vinyl aromatic monomers such as styrene, α -

methyl styrene and the like, with propylene being the α -olefin of choice.

The optional diene monomer(s) can be conjugated or nonconjugated. Conjugated monomers include butadiene,
5 isoprene, 2,3-dimethylbutadiene and cyclopentadiene.

Examples of suitable nonconjugated dienes include straight chain acyclic dienes such as 1,4-hexadiene, 1,5-hexadiene, 1,6-heptadiene, and, 1,7-octadiene; branched chain acyclic dienes such as 4-methyl-1,5-hexadiene, 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3-7-dimethyl-1,7-octadiene and mixed isomers of dihydromyrcene and dihydroocinene; unsubstituted and substituted cyclic dienes such as 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene; and, multicyclic dienes such as
15 tetrahydroindene, methyltetrahydroindene, dicyclopentadiene; bicyclo-(2,2,1)-hepta-2,6-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-butenyl-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene and norbornadiene. Of the dienes typically used to prepare EODEs, the preferred ones are 1,4-hexadiene, 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene, 5-methylene-2-norbornene and dicyclopentadiene and of these, 5-ethylidene-2-norbornene, 1,4-hexadiene and dicyclopentadiene are more preferred.

When employing a diene that results in little if any branching in the product elastomer, e.g., such dienes as
30 1,4-hexadiene, ethylidene-2-norbornene, dicyclopentadiene, 1-methylcyclopentadiene, indene, and the like, it can be advantageous to the properties of the product elastomer to include within the monomer mixture a diene that provides branching. Branching dienes, as they may be called, include

branched or unbranched acyclic dienes such as 1,5-hexadiene, 1,7-octadiene or 4-methyl-1,5-hexadiene; substituted or unsubstituted cyclic dienes such as cyclopentadiene, 3-methyl-1,4-cyclopentadiene, vinyl cyclohexene or norbornadiene; alkenyl-substituted norbornenes such as 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 5-propenyl-2-norbornene or 5-butenyl-2-norbornene; conjugated acyclic dienes such as butadiene, isoprene or 2,3-dimethylbutadiene; and, dialkenylaromatic dienes such as divinylbenzene.

10 The preferred elastomeric ethylene- α -olefin copolymers and EODEs can contain up to about 90, preferably from about 30 to about 85, and more preferably from about 35 to about 80, weight percent ethylene, the balance being α -olefin(s) and optional diene monomer(s). The diene
15 monomer(s), when utilized, can be incorporated into the EODE at a level of from about 0.1 to about 30, preferably from about 1 to about 25, and more preferably from about 1 to about 20, weight percent.

 Polymerization of the aforementioned monomers
20 using the catalyst of the present invention is carried out in the liquid phase, i.e., in a solution or slurry process, either continuously or in batch. These processes are generally carried out at temperatures in the range of from about -20°C. to about 300°C. and preferably from about 0°C.
25 to about 200°C., and pressures from about 5 to about 2000 psig. Dilution solvents that can be employed include straight and branched chain hydrocarbons such as the butanes, the pentanes, the hexanes, the heptanes, the octanes, and the like, cyclic and alicyclic hydrocarbons
30 such as cyclopentane, cyclohexane, cycloheptane, methylcyclopentane, methylcyclohexane, methylcycloheptane and the like, and alkyl-substituted aromatic compounds such as toluene, xylene, and the like.

A typical batch solution polymerization process can be carried out by first introducing the hydrocarbon solvent, e.g., cyclohexane, into a stirred tank reactor. The monomer feed comprising ethylene, α -olefin, e.g., propylene, and diene(s) (if utilized) is then sparged into the liquid phase. A hydrocarbon solution of the cocatalyst followed by a hydrocarbon solution of the metallocene procatalyst in the required amounts are then added to the liquid phase in the reactor. The rate of polymerization is controlled by the concentration of the catalyst. The reactor temperature is controlled by means of cooling coils, etc., and the initial total pressure in the reactor is maintained by a constant flow of gaseous monomer(s). By maintaining a faster rate of flow of gas(es) through the reactor than the rate of polymerization, the conditions in the reactor will approximate steady state conditions. The ethylene content of the elastomer product is determined by the metallocene catalyst used and by the ratio of ethylene to δ -olefin in the reactor which is controlled by manipulating the relative feed rates of these monomers to the reactor. After polymerization and deactivation of the catalyst followed by coagulation of the elastomer, the latter can be recovered by any suitable means and further processed as desired.

In a slurry polymerization process, a suspension of the solid, particulate polymer is formed in the hydrocarbon diluent to which ethylene, α -olefin(s), any optional diene(s) and the components of the catalyst composition have been added. Slurry polymerization proceeds much like solution polymerization.

Preferred polyolefin elastomers that can be obtained by the polymerization process herein possess a unique combination of high molecular weight (M_w), high Mooney viscosity ($ML_{1,4}$), low polydispersity index (M_w/M_n), low

glass transition temperature (T_g) and low hysteresis ($\tan \delta$) properties that distinguish them from known polyolefin elastomers. The novel polyolefin elastomers of this invention prior to curing possess an M_w of from about 5 200,000 to about 2,000,000, preferably from about 275,000 to about 1,750,000 and more preferably from about 300,000 to about 1,500,000, an $ML_{1,4}$ at 125°C of from about 10 to about 200, preferably from about 15 to about 175 and more preferably from about 20 to about 150, an M_w/M_n of from 10 about 1.25 to about 10, preferably from about 1.5 to about 8.5 and more preferably from about 2.0 to about 7.5, a T_g (°C) of below about -25, preferably below about -30 and more preferably below -35 and a $\tan \delta$ of from about 0.3 to about 7, preferably from about 0.35 to about 6 and more 15 preferably from about 0.4 to about 5.

These advantageous properties can be exploited in a variety of products. Thus, polymer blends can be prepared which contain an elastomer in accordance with this invention and one or more other hydrocarbon polymers with which 20 elastomers such as the EPDMs are known to be compatible, e.g., poly(α -olefin) homopolymers and copolymers, polystyrene, ethylene/cycloolefin copolymer, butyl rubber, polyisoprene, polybutadiene, and the like. The elastomer herein can be incorporated into any of a wide assortment of 25 rubber articles such as hoses, tubing, power transmission belts including V-belts, conveyor belts, timing belts and industrial flat belts, air springs, roofing membranes, weather stripping, bushings, vibration mounts, bridge bearing pads, shoe soles and heels, jacketing for wire or 30 cable, and the like. The elastomer of this invention is also useful as a viscosity modifier for lubricating oils.

To facilitate the manufacture of a polymer blend, the elastomer herein can be provided as an oil-extended polymer prior to mixing with the other hydrocarbon polymer.

The elastomer can be oil-extended by the well known procedure of adding oil to the polymer after it is recovered from the polymerization reactor. The oil can be selected from the naphthenic or paraffinic oils, typically in amounts of from about 5 to about 150 parts by weight of oil per 100 parts by weight of elastomer. Alternatively, part or all of the oil can be added to the elastomer and other hydrocarbon polymer during the blending operation.

The elastomer of this invention can be formulated in a known manner with any of the many usual compounding ingredients, for example, a vulcanizing or curative package containing one or more vulcanizing agents, accelerators, activators, retarders, and the like. Other common formulation ingredients include antiozonants, antioxidants, plasticizing oils and softeners, fillers, reinforcing pigments and carbon blacks.

EXAMPLES

The examples that follow include those that are illustrative of the invention (Examples 1-27) and those that are illustrative of known polymerization processes, catalysts and elastomers (Comparative Examples 1-48). The procatalysts, MAO cocatalyst, cation-generating cocatalyst components, solvents and monomers employed in these examples are as follows:

1. bis(cyclopentadienyl)zirconium dichloride [Cp₂ZrCl₂]
2. diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride [Ph₂C(Cp-9-Flu)ZrCl₂]
3. diphenylsilyl(cyclopentadienyl)(fluorenyl)zirconium dichloride [Ph₂Si(Cp-9-Flu)ZrCl₂]
4. diphenylmethylene(cyclopentadienyl)(indenyl)zirconium dichloride [Ph₂C(Cp-9'-Ind)ZrCl₂]
5. diphenylsilyl(cyclopentadienyl)(indenyl)zirconium dichloride [Ph₂Si(Cp-9'-Ind)ZrCl₂]

6. dimethylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride $[\text{Me}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2]$
7. racemic-dimethylsilylbis(2-methylindenyl)zirconium dichloride $[\text{rac-Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2]$
- 5 8. dimethylsilylbis(cyclopentadienyl)zirconium dichloride $[\text{Me}_2\text{Si}(\text{Cp})_2\text{ZrCl}_2]$
9. dimethylsilylbis(fluorenyl)zirconium dichloride $[\text{Me}_2\text{Si}(\text{Flu})_2\text{ZrCl}_2]$
- 10 10. racemic-ethylenebis(indenyl)zirconium dichloride $[\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2]$
11. racemic-dimethylsilylbis(indenyl)zirconium dichloride $[\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2]$
12. racemic-ethylenebis(indenyl)hafnium dichloride $[\text{rac-Et}(\text{Ind})_2\text{HfCl}_2]$
- 15 13. racemic-dimethylsilylbis(indenyl)hafnium dichloride $[\text{rac-Me}_2\text{Si}(\text{Ind})_2]$
14. dimethylsilyl(tetramethylcyclopentadienyl)(t-butyl-amido)titanium dichloride $[\text{Me}_2\text{Si}(\text{Cp}^*)(\text{NBu}^t)\text{TiCl}_2]$
15. tris(pentafluorophenyl)borane $[\text{B}(\text{C}_6\text{F}_5)_3]$
- 20 16. trityl tetrakis(pentafluorophenyl)borate $[\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4]$
17. dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{HNMe}_2\text{PhB}(\text{C}_6\text{F}_5)_4]$
18. lithium tetrakis(pentafluorophenyl)borate $[\text{LiB}(\text{C}_6\text{F}_5)_4]$
19. methyl aluminoxane $[\text{MAO}]$
- 25 20. triisobutylaluminum $[\text{Al}(\text{Bu}^i)_3]$, 25 weight % Al in hexanes, 0.86M Al

Hexane solvent was purified over 3 Å molecular sieves. Toluene solvent was distilled from molten sodium and degassed with dry, deoxygenated argon. Ethylene and

30 propylene, both high purity grade monomers, were purified by passage over molecular sieves and a deoxygenation catalyst. The diene monomers 5-ethylidene-2-norbornene [ENB], dicyclopentadiene [DCPD], 5-vinyl-2-norbornene [VNB] and

1,7-octadiene [OD] were deinhibited over activated alumina and stored over 4 Å molecular sieves.

The following procedures were used to determine the properties of the elastomers.

5

Weight Average Molecular Weight (M_w),
Number Average Molecular Weight (M_n) and (M_w/M_n)

The molecular weights of the elastomers, M_w and M_n , were measured in orthodichlorobenzene at 130°C on a
10 Waters GPC 150C gel permeation chromatograph equipped with a Waters RA401 refractive index detector and Waters Styragel HT columns (10E5 Å, 10E4 Å, 10E3 Å, and 10E6 Å). Molecular weights were calculated from elution times calibrated against polystyrene standards from American Polymer
15 Standards Corp. (narrow molecular weight distribution, M_n from 9300 to 2.1×10^6).

Mooney Viscosity ($ML_{1,4}$ at 125°C)

The Mooney viscosity of the elastomers, $ML_{1,4}$ at
20 125°C, was measured on a Monsanto Mooney Viscometer model MV 2000 according to ASTM standard D1646.

Glass Transition Temperature (T_g)

The glass transition temperatures of the
25 elastomers (T_g) were measured by differential scanning calorimetry upon 20-25 mg of polymer molded at 150°C for 15 minutes followed by annealing at room temperature for 24 h. T_g is reported as the midpoint of the glass transition on the heating curve of the sample, recorded on a Perkin Elmer
30 DSC 7 differential scanning calorimeter (from -100°C to 180°C at a heating rate of 20°C/minute).

Hysteresis ($\tan \delta$)

The hysteresis of the elastomers ($\tan \delta$; ASTM standard D945) was determined using a Monsanto Rubber Process Analyzer model RPA 2000 and is reported as the average of ten measurements made at 150°C at a frequency of 0.25 rad/s and at a strain of 1° arc (14%).

Ethylene:Propylene Ratio and Diene Content

The ethylene:propylene ratio and the diene content of the elastomers were determined by infrared spectroscopy of thin polymer films on a Perkin-Elmer infrared spectrophotometer model Paragon 1000 PC, according to ASTM standard D3900.

General Solution Polymerization Procedure A (Employing an MAO Cocatalyst)

The metallocene procatalyst was tared into a hypovial and combined with vigorous mixing under argon with the appropriate aliquot of MAO solution. The resulting catalyst solution was aged for 30 minutes prior to use. In one polymerization run, 0.056 grams (100 micromoles) of diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride [$\text{Ph}_2\text{C}(\text{Cp-9-Flu})\text{ZrCl}_2$] was reacted with 40.0 ml of MAO solution. This yielded a catalyst solution with $\text{Zr}=2.0$ mM and an Al/Zr ratio of 1250.

Next, a 2-liter glass reactor was charged with 1500 ml of hexane, 1.2 ml $\text{Al}(\text{Bu}^i)_3$, equivalent to 1.0 mmol Al, the appropriate aliquots of diene, and 50 psi each of ethylene and propylene (mass flow ratio determined on rotameters) and allowed to thermally equilibrate.

The catalyst solution was then injected into the reactor. Ethylene and propylene were supplied on demand to maintain reactor pressure at 50 psi. The polymerization was terminated with 100 ml of acidified methanol (one volume

%concentrated HCl) and the resulting polymer was coagulated and thereafter mill-dried.

5 General Solution Polymerization Procedure B
 (Employing A Cation-generating Cocatalyst)

 A 2-liter glass reactor was charged with 1500 ml of hexane, 1.2 ml of $\text{Al}(\text{Bu}^i)_3$ (1.0 mmol Al), the appropriate aliquots of diene and 50 psi each of ethylene and propylene (mass flow ratio determined on rotameters) and allowed to thermally equilibrate. The catalyst, 1.0 ml of a 10 mM solution of $\text{Ph}_2\text{C}(\text{Cp-9-Flu})\text{ZrCl}_2$ (0.056 g, 100 micromoles in 10 ml toluene), was injected into the reactor and allowed to react with the $\text{Al}(\text{Bu}^i)_3$ for 2 minutes.

 The remaining components of the cocatalyst, e.g., 1.0 ml of a 10 mM solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.102g, 100 micromol) and $\text{LiB}(\text{C}_6\text{F}_5)_4$ (0.152 g, 100 micromol) in 10 ml of toluene, were injected into the reactor. Ethylene and propylene were supplied on demand to maintain the reactor pressure at 50 psi. Polymerization was terminated with 100 ml of acidified methanol (1 vol % concentrated HCl) and the resulting polymer was coagulated and thereafter mill-dried.

 The polymer products were analyzed by IR spectroscopy to determine the E:P ratio and diene content. In addition, for most samples, molecular weight (M_w) thermal transitions (DSC), $\tan \delta$, and Mooney viscosity at 125°C were determined.

 The specific polymerization conditions and physical properties of the resulting polymers for each of the examples are summarized in Tables 1-6, infra.

30

COMPARATIVE EXAMPLES 1-19

 Employing solution polymerization procedure A described above, several MAO-activated bridged metallocene catalysts whose bridging groups lack bulky groups were

utilized for the attempted preparation of EP and EPDM-type elastomers. The conditions of each polymerization and the properties of the resulting polymers are summarized below in Table 1.

TABLE 1: COMPARATIVE EXAMPLES 1-19

A. POLYMERIZATION CONDITIONS AND RESULTS

COMP. EX.	PROCATALYST M	$\mu\text{mol M}$	T ($^{\circ}\text{C}$)	FEED E:P	DIENE TYPE	mL	mmol Al (Bu) ₃	mmol Al (MAO)	MAO/M	TIME (min)	YIELD (g)	ACTIVITY kg/qZr/h
1	rac-Et(Ind) ₂ ZrCl ₂	2.5	40	2:1	--	--	1.0	2.8	1000	10	79	2009
2	rac-Et(Ind) ₂ ZrCl ₂	10.0	40	2:1	ENB	10.0	1.0	11.2	1000	10	204	1292
3	rac-Et(Ind) ₂ ZrCl ₂	10.0	40	2:1	DCPD	10.0	1.0	11.2	1000	10	110	695
4	rac-Et(Ind) ₂ HfCl ₂	25.0	40	1:1	--	--	1.0	42.0	1500	30	68	31
5	rac-Et(Ind) ₂ HfCl ₂	50.0	40	1:1	ENB	5.0	1.0	28.0	500	30	100	22
6	rac-Et(Ind) ₂ HfCl ₂	50.0	40	1:1	DCPD	5.0	1.0	28.0	500	30	87	20
7	rac-Me ₂ Si(Ind) ₂ ZrCl ₂	2.5	40	2:1	--	--	1.0	2.2	872	10	83	2171
8	rac-Me ₂ Si(Ind) ₂ ZrCl ₂	10.0	40	2:1	ENB	10.0	1.0	8.7	872	10	147	966
9	rac-Me ₂ Si(Ind) ₂ ZrCl ₂	10.0	40	2:1	DCPD	10.0	1.0	8.7	872	10	43	281
10	rac-Me ₂ Si(Ind) ₂ HfCl ₂	50.0	40	2:1	--	--	1.0	43.6	872	30	67	15
11	rac-Me ₂ Si(Ind) ₂ HfCl ₂	100.0	40	2:1	ENB	10.0	1.0	87.2	872	30	36	4
12	rac-Me ₂ Si(Ind) ₂ HfCl ₂	100.0	40	2:1	DCPD	10.0	1.0	87.2	872	30	32	4
13	rac-Me ₂ Si(2-MeInd) ₂ ZrCl ₂	2.0	40	2:1	--	--	1.0	3.1	1560	10	53	1718
14	rac-Me ₂ Si(2-MeInd) ₂ ZrCl ₂	16.0	40	2:1	ENB	5.0	1.0	12.5	1560	15	32	88
15	rac-Me ₂ Si(2-MeInd) ₂ ZrCl ₂	16.0	40	2:1	DCPD	5.0	1.0	12.5	1560	15	10	28
16	Me ₂ Si(Flu) ₂ ZrCl ₂	2.6	40	2:1	--	--	1.0	2.8	1080	10	147	3714
17	Me ₂ Si(Flu) ₂ ZrCl ₂	10.4	40	2:1	ENB	5.0	1.0	11.2	1080	10	77	461
18	Me ₂ Si(Flu) ₂ ZrCl ₂	10.4	40	2:1	DCPD	5.0	1.0	11.2	1080	10	77	486
19	Me ₂ C(Cp*-Flu)ZrCl ₂	20.0	40	1:1	--	--	1.0	20.6	1030	30	91	99

*Added to reduce the MAO/Zr AND MAO/Hf ratios.

B. POLYMER PROPERTIES

COMP. EX.	M _n x10 ⁻³	M _w /M _n	ML _n (125 $^{\circ}\text{C}$)	POLYMER E:P	DIENE (wt%)	T _g ($^{\circ}\text{C}$)	tan δ	COMMENT
1	161	1.85	low	82:18	--	-39	n.d.	Low Mooney
2	142	2.15	low	69:31	6.6	-49	n.d.	Low Mooney
3	159	1.92	low	80:20	9.9	-31	n.d.	Low Mooney
4	616	2.06	90	59:41	--	-57	n.d.	Low activity
5	514	2.19	70	59:41	3.7	-52	n.d.	Low activity
6	582	2.37	91	59:41	4.5	-51	n.d.	Low activity
7	188	2.03	low	76:24	--	-38	n.d.	Low Mooney
8	164	2.07	low	70:30	4.9	-45	n.d.	Low Mooney
9	197	1.83	low	80:20	11.0	-28	n.d.	Low Mooney
10	443	2.31	n.d.	65:35	--	-55	n.d.	Low activity
11	162	2.02	low	68:32	12.1	-42	n.d.	Low activity
12	213	1.84	low	69:31	13.6	-38	n.d.	Low activity
13	336	1.98	35	80:20	--	-39	2.7	--
14	330	1.86	45	78:22	0.0	-38	2.9	No diene incorporation; diene inhibition of activity
15	320	1.89	n.d.	79:21	0.0	-38	3.4	No diene incorporation; diene inhibition of activity
16	486	2.05	52	68:32	--	-58	n.d.	--
17	477	1.96	48	83:17	0.0	-61	n.d.	No diene incorporation; diene inhibition of activity
18	409	1.95	43	79:21	0.0	-58	n.d.	No diene incorporation; diene inhibition of activity
19	44	1.92	low	58:42	--	n.d.	n.d.	Low Mooney, low activity

As these data show, Comparative Examples 1-3 and 7-9 illustrating the use of zirconium-based metallocene catalysts yielded low Mooney viscosity polymers and Comparative Examples 4-6 and 10-12 illustrating the use of hafnium-based metallocene catalysts exhibited unacceptably low activity. All of the catalysts employed in Comparative Examples 1-13 showed relatively poor activity toward propylene. Comparative Examples 13-18 yielded copolymers only, not terpolymers; there was no diene incorporation and diene inhibition was observed. Comparative Example 19 showed low catalyst activity and the resulting elastomer possessed low Mooney viscosity.

EXAMPLES 1-3

Employing solution polymerization procedure A described above, MAO-activated bridged metallocene catalysts whose bridging groups possess two bulky groups were utilized for the production of elastomers. The conditions of each polymerization and the properties of the resulting elastomers are summarized in Table 2.

TABLE 2: EXAMPLES 1-3

A. POLYMERIZATION CONDITIONS

EX.	PROCATALYST M	μmol M	T (°C)	FEED E:P	DIENE TYPE	mL	mmol Al (Bu) ¹ ,*	mmol Al (MAO)	MAO/ M
1	Ph ₂ C(Cp-9-Flu)ZrCl ₂	10.0	40	2:1	--	--	1.0	25.0	2500
2	Ph ₂ C(Cp-9-Flu)ZrCl ₂	10.0	40	2:1	ENB	10.0	1.0	25.0	2500
3	Ph ₂ C(Cp-9-Flu)ZrCl ₂	10.0	40	2:1	DCPD	10.0	1.0	25.0	2500

*Added to reduce the MAO/Zr ratios.

B. POLYMERIZATION RESULTS AND POLYMER PROPERTIES

EX.	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/h	M_n $\times 10^{-3}$	M_w/M_n	M_L , (125°C)	POLYMER E:P	DIENE (wt%)	T _g (°C)	tan δ	COMMENT
1	15	99	433	260	1.92	22	71:29	--	-43	n.d.	High MAO/Zr required for good results
2	15	90	394	232	2.00	20	70:30	7.2	-41	n.d.	High MAO/Zr required for good results
3	15	92	403	232	2.02	21	71:29	6.9	-39	n.d.	High MAO/Zr required for good results

In these examples, the yields were high and good E:P ratio were consistently achieved. In Examples 2 and 3, diene was successfully incorporated into the polymers to provide EPDM elastomers. All of the elastomers exhibited good properties. Examples 1 to 3 also demonstrate the typically high ratios of MAO to metallocene that are needed for good results.

EXAMPLES 4-9

The polymerization procedures used in these examples are similar to those employed in Examples 1-3 and are intended to show the beneficial effects of employing an additional diene monomer as a branching agent upon certain of the properties of the resulting EPDM-type elastomers, specifically, their Mooney viscosity, M_w , M_w/M_n and $\tan \delta$ values. The conditions of each polymerization and the properties of the resulting polymers are summarized in Table 3.

TABLE 3: EXAMPLES 4-9

A. POLYMERIZATION CONDITIONS											
EX.	PROCATALYST M	μmol M	T (°C)	FEED E:P	DIENE TYPE	mL	BRANCHING AGENT TYPE	mL	mmol Al (Bu^t) ₃	mmol Al (MAO)	MAO/ M
4	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	70	2:1	ENB	5.0	--	--	1.0	25.0	2500
5	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	70	2:1	ENB	4.88	VNB	0.12	1.0	25.0	2500
6	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	70	2:1	ENB	4.75	VNB	0.25	1.0	25.0	2500
7	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	25.0	2500
8	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	40	2:1	ENB	9.5	OD	0.5	1.0	12.5	1250
9	$\text{Ph}_2\text{C}(\text{Cp}-9\text{-Flu})\text{ZrCl}_2$	10.0	70	2:1	ENB	9.5	OD	0.5	1.0	12.5	1250

B. POLYMERIZATION RESULTS AND POLYMER PROPERTIES

EX.	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/h	M_n $\times 10^{-1}$	M_w/M_n	M_L (125°C)	POLYMER E:P	DIENE (wt%)	T _g (°C)	tan δ	COMMENT
4	15	90	394	214	1.93	16	77:23	5.6	-33	4.5	High MAO/Zr required for good results
5	15	92	404	227	2.08	21	76:24	5.5	-37	1.8	High MAO/Zr required for good results
6	15	89	390	272	2.42	31	77:23	5.6	-35	0.9	High MAO/Zr required for good results
7	15	91	399	354	2.75	44	77:23	5.1	-34	0.6	High MAO/Zr required for good results
8	15	36	156	378	2.18	91	75:25	13.0	n.d.	n.d.	High MAO/Zr required for good results
9	15	34	148	291	2.26	65	77:23	16.4	n.d.	n.d.	High MAO/Zr required for good results

Examples 4 to 7 employing a MAO/metallocene ratio twice as high as that of Example 8 and 9 resulted in much greater yields and much higher activities than the latter further demonstrating the need to utilize very high MAO/metallocene ratios in order to achieve optimum process results. Examples 5 to 9 show that incorporation of a branching diene resulted in improvements in the Mooney viscosity, M_n , M_w/M_n and tan δ values (where determined) of each elastomer relative to the elastomer of Example 4 which contained no branching diene.

COMPARATIVE EXAMPLES 20-23;
EXAMPLES 10-19

Employing solution polymerization procedure B described above, metallocene catalysts whose bridging groups possess two bulky groups and which were activated by cation-generating cocatalyst both within (Examples 10-19) and outside (Comparative Examples 20-23) the scope of the invention were used for the preparation of EPDM elastomers. The conditions of each polymerization and the properties of the resulting polymers are summarized in Table 4.

TABLE 4: COMPARATIVE EXAMPLES 20-23; EXAMPLES 10-19

A. POLYMERIZATION CONDITIONS

COMP. EX. / EX.	PROCATALYST M	μmol M	T (°C)	FEED E:P	DIENE TYPE	mL	BRANCHING AGENT TYPE	mL	CATION-GENERATING mmol Al(Bu) ³	BORON CMPD(S)*	μmol B	B/M
20	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	B	20	2
21	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	Ph ₃ C	10	1
22	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	HNMe ₂ Ph	20	2
23	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	LiB	20	2
10	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	70	2:1	ENB	4.5	VNB	0.5	1.0	LiB+B	20	2
11	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	40	1:1	ENB	9.75	VNB	0.25	1.0	LiB+B	20	2
12	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	40	1.25:1	ENB	9.75	VNB	0.25	1.0	LiB+B	20	2
13	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	40	1.5:1	ENB	9.75	VNB	0.25	1.0	LiB+B	20	2
14	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	40	1.5:1	ENB	9.65	VNB	0.35	1.0	LiB+B	20	2
15	Ph ₃ C(Cp-9-Flu)ZrCl ₂	10.0	40	2:1	ENB	9.75	OD	0.25	1.0	LiB+B	20	2
16	Ph ₃ Si(Cp-9-Flu)ZrCl ₂	10.0	40	1:1	ENB	4.82	VNB	0.18	1.0	LiB+B	20	2
17	Ph ₃ Si(Cp-9-Flu)ZrCl ₂	10.0	40	1.25:1	ENB	4.82	VNB	0.18	1.0	LiB+B	20	2
18	Ph ₃ Si(Cp-9-Flu)ZrCl ₂	10.0	40	1.5:1	ENB	4.82	VNB	0.18	1.0	LiB+B	20	2
19	Ph ₃ Si(Cp-9-Flu)ZrCl ₂	10.0	40	2:1	ENB	4.82	VNB	0.18	1.0	LiB+B	20	2

*B = B(C₂F₅)₃; Ph₃C = Ph₃CB(C₂F₅)₃; HNMe₂Ph = (HNMe₂Ph)B(C₂F₅)₃; LiB = LiB(C₂F₅)₃.

B. POLYMERIZATION RESULTS AND POLYMER PROPERTIES

COMP. EX. / EX.	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/h	M _n x10 ⁻³	M _w /M _n	ML ₁₀₀ (125°C)	POLYMER E:P	DIENE (wt%)	T _g (°C)	tan δ	COMMENT
20	10	12	80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Short-lived
21	10	55	362	415	2.96	53	74.26	4.5	-37	0.53	Short-lived with very high initial activity
22	10	111	730	620	3.38	127	n.d.	n.d.	-34	n.d.	Short-lived with very high initial activity; gel formed
23	10	0	--	--	--	--	--	--	--	--	No activity
10	10	96	635	421	2.58	62	74.26	4.3	-39	0.61	Superior to those produced with MAO catalyst
11	10	99	655	233	2.47	36	52:48	7.2	-50	1.5	Superior to those produced with MAO catalyst
12	10	111	734	287	2.60	51	61:39	6.8	-49	0.89	Superior to those produced with MAO catalyst
13	10	106	705	334	2.74	62	66:34	7.4	-47	0.72	Superior to those produced with MAO catalyst
14	10	115	761	430	3.53	78	59:41	5.6	-50	n.d.	Superior to those produced with MAO catalyst
15	10	101	670	613	3.63	94	70:30	7.4	-44	0.42	Superior to those produced with MAO catalyst
16	10	75	495	699	2.20	--	66:34	3.8	-43	1.03	Mooney too high to be measured
17	10	68	453	820	2.37	--	70:30	4.3	n.d.	n.d.	Mooney too high to be measured
18	10	66	435	935	2.36	--	74:26	4.4	n.d.	n.d.	Mooney too high to be measured
19	10	74	488	928	2.39	--	77:23	4.3	n.d.	n.d.	Mooney too high to be measured

As these data show, the catalysts utilized in Comparative Examples 20-23 were short lived and resulted in little or no activity after an initial burst of high activity (the catalyst of Comparative Example 23 showed no activity at all). In contrast to these results, Examples 10-19 illustrating the use of a cation-generating cocatalyst in accordance with this invention showed consistently good activity for the entire polymerization term, a result demonstrating its much greater stability than the cation-generating cocatalysts of the comparative examples. This result is all the more surprising considering that the boron-containing compounds of the cation-generating cocatalyst of this invention when employed individually as in Comparative Examples 20 and 23 give unacceptable results.

COMPARATIVE EXAMPLES 24-43; EXAMPLES 20-24

Employing essentially the same procedures as in Comparative Examples 20-23/Examples 10-19, polymerizations were carried out with various metallocene catalysts that had been activated by cation-generating cocatalysts both within (Examples 20-24) and outside (Comparative Examples 24-43) the scope of the invention. The conditions of each polymerization and its results are summarized in Table 5.

TABLE 5: COMPARATIVE EXAMPLES 24-43; EXAMPLES 20-24

COMP. EX./ EX.	PROCATALYST	A. POLYMERIZATION CONDITIONS											COMMENT
		μmol M	T (°C)	FEED E:P	ml ENB	mmol Al (Bu) ³	CATION-GENERATING BORON CMPD(S)*	μmol B	B/M	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/H	
24	Cp,ZrCl ₂	2.5	40	1:1	5.0	1.0	B	5	2	10	7	175	Short-lived
25	Cp,ZrCl ₂	2.5	40	1:1	5.0	1.0	LiB	5	2	10	0	--	No activity
26	Cp,ZrCl ₂	2.5	40	1:1	5.0	1.0	Ph ₃ C	5	2	10	53	894	Short-lived with very high initial activity
27	Cp,ZrCl ₂	2.5	40	1:1	5.0	1.0	HNMe ₂ Ph	5	2	10	38	649	Short-lived, high initial activity
20	Cp,ZrCl ₂	2.5	40	1:1	5.0	1.0	LiB+B	5	2	10	37	631	No decrease in activity with time
28	Me ₂ Si(Cp), ZrCl ₂	10.0	40	1:1	5.0	1.0	B	20	2	10	9	58	Short-lived
29	Me ₂ Si(Cp), ZrCl ₂	10.0	40	1:1	5.0	1.0	LiB	20	2	10	5	36	Very low activity
30	Me ₂ Si(Cp), ZrCl ₂	10.0	40	1:1	5.0	1.0	Ph ₃ C	20	2	10	30	212	Short-lived with very high activity
31	Me ₂ Si(Cp), ZrCl ₂	10.0	40	1:1	5.0	1.0	HNMe ₂ Ph	20	2	10	20	139	Short-lived, high initial activity, gel
21	Me ₂ Si(Cp), ZrCl ₂	10.0	40	1:1	5.0	1.0	LiB+B	20	2	10	24	175	No decrease in activity with time
32	rac-Et(Ind), ZrCl ₂	2.5	40	1:1	5.0	1.0	B	5	2	10	10	292	Short-lived
33	rac-Et(Ind), ZrCl ₂	2.5	40	1:1	5.0	1.0	LiB	5	2	10	0	--	No activity
34	rac-Et(Ind), ZrCl ₂	2.5	40	1:1	5.0	1.0	Ph ₃ C	5	2	10	228	5642	Short-lived with very high initial activity
35	rac-Et(Ind), ZrCl ₂	2.5	40	1:1	5.0	1.0	HNMe ₂ Ph	5	2	10	169	4239	Short-lived, high initial activity, gel
22	rac-Et(Ind), ZrCl ₂	2.5	40	1:1	5.0	1.0	LiB+B	5	2	10	146	3712	No decrease in activity with time
36	Me ₂ C(Cp-9- Flu)ZrCl ₂	10.0	40	1:1	5.0	1.0	B	20	2	10	9	65	Short-lived
37	Me ₂ C(Cp-9- Flu)ZrCl ₂	10.0	40	1:1	5.0	1.0	LiB	20	2	10	0	--	No activity
38	Me ₂ C(Cp-9- Flu)ZrCl ₂	10.0	40	1:1	5.0	1.0	Ph ₃ C	20	2	10	69	467	Short-lived with very high initial activity
39	Me ₂ C(Cp-9- Flu)ZrCl ₂	10.0	40	1:1	5.0	1.0	HNMe ₂ Ph	20	2	10	46	321	Short-lived high initial activity, gel

A. POLYMERIZATION CONDITIONS (continued)

COMP. EX./ EX.	PROCATALYST	M	μmol	T (°C)	FEED E:P	mL ENB	mmol Al (Bu ³) ₃	CATION-GENERATING BORON CMPD(S)*	μmol B	B/M	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/H	COMMENTS
23	Me ₂ C(Cp*-9-Flu)ZrCl ₂		10.0	40	1:1	5.0	1.0	LiB+B	20	2	10	55	380	Slight decrease in activity with time
40	Me ₂ Si(Cp*)(NBu ³)TiCl ₂		10.0	40	1:1	5.0	1.0	B	20	2	10	8	97	Short-lived
41	Me ₂ Si(Cp*)(NBu ³)TiCl ₂		10.0	40	1:1	5.0	1.0	LiB	20	2	10	0	--	No activity
42	Me ₂ Si(Cp*)(NBu ³)TiCl ₂		10.0	40	1:1	5.0	1.0	Ph ₃ C	20	2	10	107	1149	Short-lived with very high initial activity
43	Me ₂ Si(Cp*)(NBu ³)TiCl ₂		10.0	40	1:1	5.0	1.0	HNMe ₂ Ph	20	2	10	90	1154	Short-lived, high initial activity, gel
24	Me ₂ Si(Cp*)(NBu ³)TiCl ₂		10.0	40	1:1	5.0	1.0	LiB+B	20	2	10	94	1196	No decrease in activity with time

*B = B(C₂F₅)₃; Ph₃C = Ph₃CB(C₂F₅)₃; HNMe₂Ph = (HNMe₂Ph)B(C₂F₅)₃; LiB = LiB(C₂F₅)₃.

While the Al(Bu³)₃+Ph₃C cocatalyst yields an activated metallocene catalyst with very high initial activity (Comparative Examples 26, 30, 34, 38 and 42), the activity is short-lived compared to the far more stable catalysts that are obtained by activating the metallocene procatalysts with a cation-generating cocatalyst of this invention (Examples 20-24). This difference in results is graphically shown in accompanying Figure 1 which presents a comparison in monomer consumption over time between:

5 procatalyst activated with Al(Bu³)₃+Ph₃C (Comparative Example 30) and procatalyst activated with Al(Bu³)₃+LiB+B (Example 21). The catalyst obtained with Al(Bu³)₃+Ph₃C cocatalyst lost all activity within a matter of minutes while the catalyst obtained with the Al(Bu³)₃+LiB+B cocatalyst of this

10 invention continued to provide good activity for the entire 10 minutes of polymerization indicated and well beyond.

Largely the same sort of instability observed for metallocenes obtained with the Al(Bu³)₃+Ph₃C cocatalyst was also evident in the metallocenes activated with the

15 Al(Bu³)₃+HNMe₂Ph cocatalyst of Comparative Examples 27, 31,

35 and 39), the latter exhibiting the further disadvantage of causing gelation of the polymer.

COMPARATIVE EXAMPLES 44-48; EXAMPLES 25-27

5 Comparative Examples 44-48 utilized solution polymerization procedure A and are illustrative of the use of a known type of MAO-activated catalyst. Examples 25-27 utilized solution polymerization procedure B and illustrate the use of a catalyst obtained by activating the same procatalyst employed in the comparative examples with a cation-generating cocatalyst in accordance with the invention. The conditions of the polymerizations, their results and the properties of the product polymers are summarized in Table 6.

TABLE 6: COMPARATIVE EXAMPLES 44-48; EXAMPLES 25-27

COMP. EX./EX.	PROCATALYST	M	$\mu\text{mol M}$	T (°C)	FEED E:P	DIENE		BRANCHING DIENE		MAO		CATION-GENERATING BORON		COCATALYST	
						TYPE	mL	TYPE	mL	mmol Al (MAO)	M	mmol Al (Bu ¹)	CMPD(S)*	$\mu\text{mol B}$	B/M
44	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	40	2:1	ENB	5.0	--	--	4.12	3300	1.0	--	--	--
45	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	40	2:1	ENB	4.88	VNB	0.12	4.12	3300	1.0	--	--	--
46	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	5.0	--	--	4.12	3300	1.0	--	--	--
47	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	4.88	VNB	0.12	4.12	3300	1.0	--	--	--
48	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	4.75	VNB	0.25	4.12	3300	1.0	--	--	--
25	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	5.0	--	--	--	--	1.0	LiB+B	25	2
26	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	4.75	OD	0.25	--	--	1.0	LiB+B	25	2
27	Me ₂ Si(Cp*)(NBu ¹)TiCl ₃		12.5	70	2:1	ENB	4.5	OD	0.5	--	--	1.0	LiB+B	25	2

*B = B(C₆F₅)₃; LiB = LiB(C₆F₅)₂.

B. POLYMERIZATION RESULTS AND POLYMER PROPERTIES

COMP. EX. / EX.	TIME (min)	YIELD (g)	ACTIVITY kg/gZr/h	M_n $\times 10^{-3}$	M_w/M_n	$ML_{1,4}$ (125°C)	POLYMER E:P	DIENE (wt%)	T _g (°C)	η_{inh}	COMMENT
44	30	48	326	338	2.00	42	59:41	5.8	-45	3.28	High MAO/Zr
45	30	50	337	438	2.26	72	62:38	5.6	-43	1.16	High MAO/Zr
46	15	72	484	323	2.02	37	70:30	4.1	-37	2.67	High MAO/Zr, high T _g
47	15	83	555	368	2.13	44	69:31	3.7	-38	1.75	High MAO/Zr, high T _g
48	15	74	498	384	2.21	53	71:29	3.8	-36	1.27	High MAO/Zr, high T _g
25	15	93	618	509	2.31	89	68:32	4.2	-40	1.72	Higher activity, M_n than with MAO
26	15	91	601	540	2.57	94	67:33	3.8	-40	0.54	OD very effective
27	15	92	622	598	2.77	104	68:32	3.9	-42	0.49	Little additive benefit for additional OD

When using MAO as the procatalyst (Comparative Examples 44-48), an extraordinarily high MAO/procatalyst ratio is required in order to achieve acceptable catalytic activity. Especially at a higher temperature (70°C), the reactivity of propylene is unfavorable and the T_g of the product polymer is unacceptably high. In contrast to these results, the use of the cation-generating cocatalyst of this invention to activate the procatalyst (Examples 25-27) provided higher yields and greater activities and produced polymers with better M_n , $ML_{1,4}$, and T_g.

In an alternate embodiment of this invention it is contemplated that through the use, during polymerization, of known chain transfer agents, such as hydrogen, the molecular weights of the elastomers described herein can be intentionally and substantially reduced resulting in low molecular weight, even liquid polymers which may be desirable in particular end use applications.

TABLE 7

CHARGED
TO
REACTOR

POLYMER
PROPERTIES

Examples'	DIENE	mL	α -OLEFIN	mL	E:P	wt.% DIENE	wt.% α -OLEFIN ^c	ML _{1,3} (125°C)	COMMENT
28	ENB	25	--	--	65:35	20.1	--	65	Linear
29	DCPD	15	--	--	67:33	15.2	--	68	Linear
30	ENB	10	OCTENE	10	65:35	6.1	8.2	39	Slightly Branched
31	ENB	5	ISOPRENE	10	68:32	3.0	6.4	86	Branched
32	ENB	10	STYRENE	10	69:31	6.1	5.7	67	Slightly Branched
33	ENB	20	OCTENE	30	b	15.3	26	22	Slightly Branched

NOTES: a Polymerization conditions: 1500mL hexanes, 40°C, 1:1 mass flow ratio of ethylene:propylene at 50 psig, triisobutyl aluminum=0.67 mM, [Ph₂Cp-9-Flu)ZrCl₂]=[LiB(C₆F₅)₄]=[B(C₆F₅)₃]=6.67 microM.

Polymerization duration = 10 min. Other conditions described in General Solution Polymerization Procedures on pg. 30

b No propylene

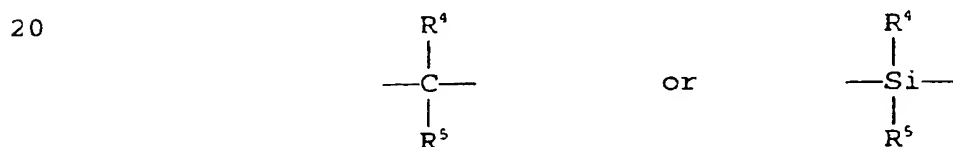
c Estimated by FTIR

WHAT IS CLAIMED IS:

1. A process for the liquid phase polymerization of ethylene, at least one other α -olefin and, optionally, at least one diene monomer to provide an elastomer, the process comprising polymerizing the monomer under liquid phase polymerization conditions in the presence of a catalytically effective amount of catalyst comprising the product obtained by combining a metallocene procatalyst with a cocatalyst, the metallocene procatalyst being at least one compound of general formulae (I) and/or (II):
- $$\begin{array}{ll} (\text{Cp}^1\text{R}^1_m)\text{R}^3_n(\text{Cp}^2\text{R}^2_p)\text{MX}_q & \text{(I)} \\ (\text{Cp}^1\text{R}^1_m)\text{R}^3_n\text{Y}_r\text{MX}_s & \text{(II)} \end{array}$$
- wherein Cp^1 of ligand $(\text{Cp}^1\text{R}^1_m)$ and Cp^2 of ligand $(\text{Cp}^2\text{R}^2_p)$ are the same or different cyclopenta-dienyl rings, R^1 and R^2 each is, independently, halogen or a hydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, m is 0 to 5, p is 0 to 5 and two R^1 and/or R^2 substituents on adjacent carbon atoms of the cyclopentadienyl ring associated therewith can be joined together to form a ring containing from 4 to about 20 carbon atoms, R^3 is a bridging group, n is 0 or 1, Y is a heteroatom-containing ligand in which the heteroatom is coordinated to M , M is a transition metal having a valence of from 3 to 6, each X is a non-cyclopentadienyl ligand and is, independently, halogen or a hydrocarbyl, oxyhydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid, oxyhydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, q is equal to the valence of M minus 2, r has the value of n and s is equal to the valence of M minus 1 when r is 0 and is equal to the valence of M minus 2 when r is 1, the cocatalyst being an aluminoxane or a cation-generating cocatalyst comprising: a metal- and/or metalloid-containing first component capable of exchanging at least

one X ligand in the metallocene procatalyst up to the total number thereof with, independently, a hydrogen atom, or a carbohydryl group containing up to about 20 carbon atoms or an oxycarbohydryl group containing up to 20 carbon atoms; a
 5 neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing
 10 constituent, provided, that when the metallocene procatalyst is one of formula (I) and the cocatalyst is entirely an aluminoxane, ligand (Cp^1R_m^1) is different from ligand (Cp^2R_p^2), bridging group R^3 contains at least two bulky groups and n is 1 and when the procatalyst is entirely one
 15 of formula (II), the cocatalyst comprises the cation-generating cocatalyst.

2. The process of Claim 1 wherein in metallocene procatalyst (I), bridging group R^3 possesses the structure



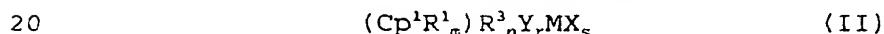
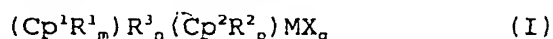
in which bulky groups R^4 and R^5 each, independently, is, or contains, a cyclohydrocarbyl group containing up to about 20 carbon atoms and from 0 to 3 heteroatoms.

30 3. The process of Claim 2 wherein the cyclohydrocarbyl group is a cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, heteroaryl, alkaryl, alkylheteroaryl, aralkyl or heteroaralkyl group.

35 4. In a process for polymerizing at least one olefin to provide a polyolefin employing, as polymerization catalyst, the product obtained by combining a metallocene procatalyst possessing at least one non-cyclopentadienyl

ligand X coordinated to its transition metal with an aluminoxane cocatalyst, wherein the improvement comprises substituting part or all of the aluminoxane cocatalyst with a cation-generating cocatalyst comprising: a metal- and/or
 5 metalloid-containing first component capable of exchanging one or more ligands X up to the full number thereof with, independently, a hydrogen atom, a carbohydryl group containing up to about 20 carbon atoms or an oxyhydrocarbyl group containing up to 20 carbon atoms; a neutral metal-
 10 and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent.

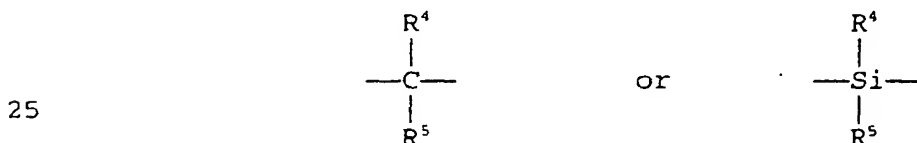
15 5. A catalyst comprising the product obtained by combining a metallocene procatalyst with a cation-generating cocatalyst, the metallocene procatalyst being one or more compounds of general formulae (I) and/or (II):



wherein Cp^1 of ligand $(\text{Cp}^1\text{R}^1_m)$ and Cp^2 of ligand $(\text{Cp}^2\text{R}^2_p)$ are the same or different cyclopenta-dienyl rings, R^1 and R^2 each is, independently, halogen or a hydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid or
 25 halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, m is 0 to 5, p is 0 to 5 and two R^1 and/or R^2 substituents on adjacent carbon atoms of the cyclopentadienyl ring associated therewith can be joined together to form a ring containing from 4 to about 20 carbon
 30 atoms, R^3 is a bridging group, n is 0 or 1, Y is a heteroatom-containing ligand in which the heteroatom is coordinated to M , M is a transition metal having a valence of from 3 to 6, each X is a non-cyclopentadienyl ligand and is, independently, halogen or a hydrocarbyl, oxyhydrocarbyl,
 35 halocarbyl, hydrocarbyl-substituted organometalloid,

oxyhydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, q is equal to the valence of M minus 2, r has the value of n and s is equal to the valence of M minus 1 when r is 0 and is equal to the valence of M minus 2 when r is 1, the cation-generating cocatalyst comprising: a metal- and/or metalloid-containing first component capable of exchanging at least one X ligand in the metallocene procatalyst up to the total number thereof with, independently, a hydrogen atom or a carbohydryl group containing up to about 20 carbon atoms or oxycarbohydryl group containing up to 20 carbon atoms; a neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent.

6. The catalyst of Claim 5 wherein in metallocene procatalyst (I), bridging group R³ possesses the structure



in which bulky groups R⁴ and R⁵ each, independently, is, or contains, a cyclohydrocarbyl group containing up to about 20 carbon atoms and from 0 to 3 heteroatoms.

7. The catalyst of Claim 6 wherein the cyclohydrocarbyl group is a cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, heteroaryl, alkaryl, alkylheteroaryl, aralkyl or heteroaralkyl group.

8. The catalyst of Claim 7 wherein ligand (Cp¹R_m¹) is unsubstituted cyclopentadienyl, ligand (Cp²R_p²) is

indenyl or fluorenyl, M^1 is zirconium, R^4 and R^5 each ligand is phenyl and each X is chlorine.

9. The catalyst of Claim 5 wherein in metallocene procatalyst (II), n and r are both 1, the
5 valence of M is 4, ligand X is halogen and s is 2.

10. The catalyst of Claim 5 wherein in the cation-generating cocatalyst, the first component is an aluminum compound, the second component is a borane compound and the third component is a metal borate compound.

10 11. The catalyst of Claim 10 wherein the aluminum compound is a trialkylaluminum or dialkylaluminum hydride, the borane compound is a tris(haloaryl)borane and the metal borate compound is an alkali metal-, alkaline earth metal-,
15 transition metal- or metalloid tetrakis(haloaryl)borate.

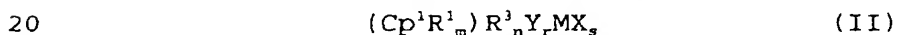
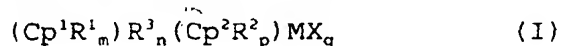
15 12. The catalyst of Claim 11 wherein the aluminum compound is a trialkylaluminum, the borane compound is a tris(halophenyl)borane and the metal borate compound is an alkali metal tetrakis(halophenyl)borate.

20 13. A cation-generating cocatalyst for activating a metallocene procatalyst, the cocatalyst comprising a metal- and/or metalloid-containing first component capable of exchanging one or more non-cyclopentadienyl ligands coordinated to the transition metal of the metallocene up to the full number of such ligands present with, independently,
25 a hydrogen atom, a carbohydryl group containing up to about 20 carbon atoms or an oxyhydrocarbyl group containing up to 20 carbon atoms; a neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent;
30 and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent.

35 14. In a catalyst comprising the product obtained by combining a metallocene procatalyst possessing at least one non-cyclopentadienyl ligand X coordinated to its

transition metal with an aluminoxane cocatalyst, wherein the improvement comprises substituting part or all of the aluminoxane cocatalyst with a cation-generating cocatalyst comprising: a metal- and/or metalloid-containing first component capable of exchanging one or more ligands X up to the full number thereof with, independently, a hydrogen atom, a carbohydryl group containing up to about 20 carbon atoms or an oxyhydrocarbyl group containing up to 20 carbon atoms; a neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent.

15 15. A process for the activation of a metallocene procatalyst with a cation-generating cocatalyst, the metallocene procatalyst being at least one compound of general formulae (I) and/or (II):



wherein Cp^1 of ligand $(\text{Cp}^1\text{R}^1_m)$ and Cp^2 of ligand $(\text{Cp}^2\text{R}^2_p)$ are the same or different cyclopenta-dienyl rings, R^1 and R^2 each is, independently, halogen or a hydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, m is 0 to 5, p is 0 to 5 and two R^1 and/or R^2 substituents on adjacent carbon atoms of the cyclopentadienyl ring associated therewith can be joined together to form a ring containing from 4 to about 20 carbon atoms, R^3 is a bridging group, n is 0 or 1, Y is a heteroatom-containing group in which the heteroatom is coordinated to M , M is a transition metal having a valence of from 3 to 6, each X is a non-cyclopentadienyl ligand and is, independently, halogen or a hydrocarbyl, oxyhydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid,

oxyhydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to about 20 carbon atoms, q is equal to the valence of M minus 2, r has the value of n and s is equal to the valence of M minus 1 when r is 0 and is equal to the valence of M minus 2 when r is 1, the cation-generating cocatalyst comprising: a metal- and/or metalloid-containing first component capable of exchanging at least one X ligand in the metallocene procatalyst up to the total number thereof with, independently, a hydrogen atom or a carbohydryl group containing up to about 20 carbon atoms or oxycarbohydryl group containing up to 20 carbon atoms; a neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal- and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent, the process comprising combining the metallocene procatalyst with the components of the cation-generating cocatalyst in any combination or in any order thereof in the presence of olefin.

16. In a process for activating a metallocene procatalyst with an aluminoxane cocatalyst to provide a metallocene catalyst, wherein the improvement comprises substituting part or all of the aluminoxane cocatalyst with a cation-generating cocatalyst comprising: a metal- and/or metalloid-containing first component capable of exchanging one or more non-cyclopentadienyl ligands coordinated to the transition metal of the metallocene up to the full number of such ligands present with, independently, a hydrogen atom, a carbohydryl group containing up to about 20 carbon atoms or an oxyhydrocarbyl group containing up to 20 carbon atoms; a neutral metal- and/or metalloid-containing second component having at least one aryl group possessing at least one electron-withdrawing substituent; and, an anionic metal-

and/or metalloid-containing third component having at least one aryl group possessing at least one electron-withdrawing substituent.

5 17. An elastomer obtained from process for the liquid phase polymerization of ethylene of claim 1.

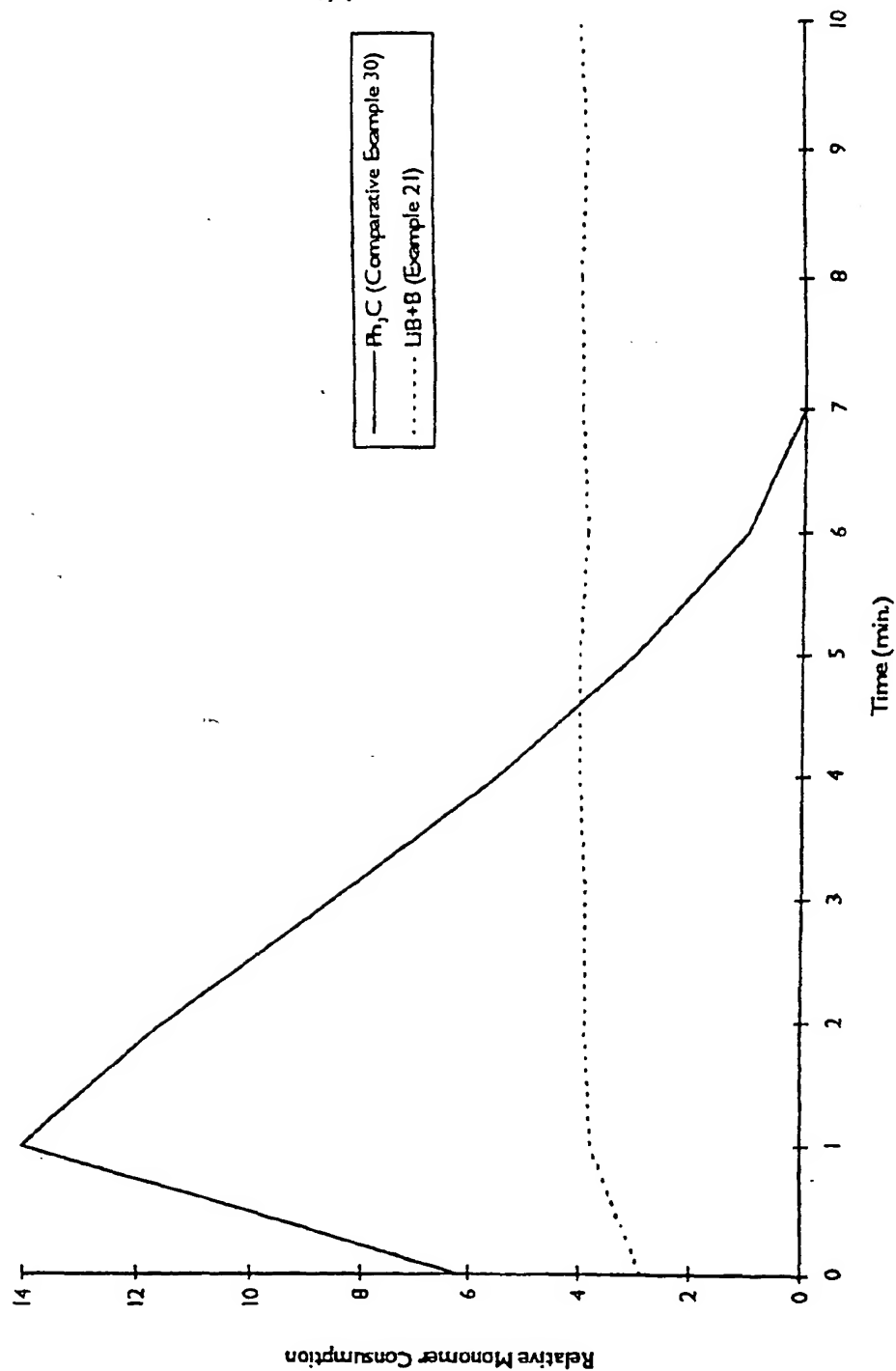
18. An elastomer obtained from the polymerization of ethylene, at least one other α -olefin and, optionally, at least one diene, the elastomer possessing an M_w of from about 200,000 to about 2,000,000, an $ML_{1,4}$ at 125°C of from about 10 to about 200, an M_w/M_n of from about 1.25 to about 10, a T_g of below about -25°C and a $\tan \delta$ of from about 0.3 to about 7.

19. A lubricating oil containing a viscosity-modifying amount of an elastomer of Claim 18.

15 20. A rubber article containing the elastomer of Claim 18, said rubber article being selected from a hose, power transmission belt, conveyor belt, gasket, fabric coating, automotive bumper, air spring, shoe sole, shoe heel, roofing membrane, jacketing for wire or cable or
20 weather stripping.

1/1

Figure 1: Monomer Consumption vs. Time



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/05323

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/06 C08F4/605 C08F210/16 C08F210/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 552 945 A (MITSUBI) 28 July 1993 see examples 10,11 see claim 1 ---	1
X	WO 93 25591 A (SPHERILENE) 23 December 1993 see claims 1,3-5 see example 9 ---	1
X	EP 0 668 295 A (UNION CARBIDE) 23 August 1995 see page 8, line 48 - page 10, line 16 see page 12; table 2 see example SL17 --- -/-	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

28 July 1997

Date of mailing of the international search report

20.08.97

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Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/05323

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 570 982 A (TOSOH) 24 November 1993	4,5, 10-16
Y	see claims 1,9	1
Y	see page 6 - page 8; examples 1-4	
Y	see page 6, line 10 - line 18	1
X	EP 0 347 129 A (EXXON) 20 December 1989 cited in the application see page 12; examples 27,28	18
P,X	EP 0 754 698 A (MITSUI) 22 January 1997 see page 48; example 14 see page 21, line 10 - line 27	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/05323

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Information on patent family members

International Application No

PCT/US 97/05323

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DUPLEX



A DOCPHOENIX

APPL PARTS



371P
PCT Papers in a 371 Application

A...
Amendment Including Elections

ABST
Abstract

ADS
Application Data Sheet

AF/D
Affidavit or Exhibit Received

APPENDIX
Appendix

ARTIFACT
Artifact

BIB
Bib Data Sheet

CLM
Claim

COMPUTER
Computer Program Listing

CRFL
All CRF Papers for Backfile

DIST
Terminal Disclaimer Filed

DRW
Drawings

5/06/02 FOR 28
Foreign Reference

FRPR
Foreign Priority Papers

IDS
IDS Including 1449

NPL
Non-Patent Literature

OATH
Oath or Declaration

PET.
Petition

RETMAIL
Mail Returned by USPS

SEQLIST
Sequence Listing

SPEC
Specification

SPEC NO
Specification Not in English

TRNA
Transmittal New Application

CTNF
Count Non-Final

CTRS
Count Restriction

EXIN
Examiner Interview

M903
DO/EO Acceptance

M905
DO/EO Missing Requirement

NFDR
Formal Drawing Required

NOA
Notice of Allowance

PETDEC
Petition Decision

OUTGOING



1449
Signed 1449

892
892

ABN
Abandonment

APDEC
Board of Appeals Decision

APEA
Examiner Answer

CTAV
Count Advisory Action

CTEQ
Count Ex parte Quayle

CTFR
Count Final Rejection

INCOMING

AP.B
Appeal Brief

C.AD
Change of Address

N/AP
Notice of Appeal

PA..
Change in Power of Attorney

REM
Applicant Remarks in Amendment

XT/
Extension of Time filed separate

BACKFILE DOCUMENT INDEX SHEET

Internal

SRNT
Examiner Search Notes

CLMPTO
PTO Prepared Complete Claim Set

ECBOX
Evidence Copy Box Identification

WCLM
Claim Worksheet

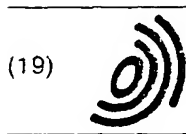
WFEE
Fee Worksheet

File Wrapper

FWCLM
File Wrapper Claim

IIFW
File Wrapper Issue Information

SRFW
File Wrapper Search Info



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(11) EP 1 148 115 A1

(12)

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(30) Priority: 09.12.1998 JP 35027998

09.12.1998 JP 35028098

(74) Representative: HOFFMANN - EITLE

Patent- und Rechtsanwälte

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(54) **VISCOSITY MODIFIER FOR LUBRICATING OIL AND LUBRICATING OIL COMPOSITION**

(57) The present invention is intended to obtain a viscosity modifier for a lubricating oil, by the use of which a lubricating oil composition of excellent low-temperature properties can be obtained, and to obtain a lubricating oil composition of excellent low-temperature properties containing the viscosity modifier. The viscosity modifier for a lubricating oil comprises an ethylene/propylene copolymer (A) having the properties: the density is in the range of 857 to 882 kg/m³, Mw is in the range of 80,000 to 400,000, Mw/Mn is not more than 2.3, and the density (D (kg/m³)) and the melting point (Tm (°C)) satisfy the relation $Tm \leq 1.247 \times D - 1037$; or comprises an ethylene/propylene copolymer (B) having the properties: the ethylene content is in the range of 70

to 79 wt%, Mw is not less than 80,000 and less than 250,000, Mw/Mn is not more than 2.3, Tm is in the range of 15 to 60°C, and the ethylene content (E (wt%)) and the melting point (Tm (°C)) satisfy the relation $3.44 \times E - 206 \geq Tm$; or comprises an ethylene/propylene copolymer (C) having the properties: the ethylene content is in the range of 70 to 79 wt%, Mw is in the range of 250,000 to 400,000, Mw/Mn is not more than 2.3, Tm is in the range of 15 to 60°C, and the ethylene content (E (wt%)) and the melting point (Tm (°C)) satisfy the relation $3.44 \times E - 204 \geq Tm$. The lubricating oil composition comprises the ethylene/propylene copolymer (A) (B) or (C), a lubricating oil base (D), and if necessary, a pour point depressant.

EP 1 148 115 A1

Description

TECHNICAL FIELD

5 [0001] The present invention relates to a viscosity modifier for a lubricating oil and a lubricating oil composition. More particularly, the invention relates to a viscosity modifier for a lubricating oil capable of producing a lubricating oil composition having excellent low-temperature properties and a lubricating oil composition containing the viscosity modifier.

BACKGROUND ART

10 [0002] The viscosity of petroleum products generally varies greatly with temperature, and for lubricating oils for automobiles, the temperature dependence of the viscosity is desired to be small. In recent years, therefore, an ethylene/ α -olefin copolymer has been widely used as a viscosity modifier having an effect of improving viscosity index for the purpose of decreasing the temperature dependence of the lubricating oils.

15 [0003] When the surrounding temperature lowers, a wax component in a lubricating oil is crystallized and solidified to make the lubricating oil lose flowability, so that a pour point depressant is also contained in the lubricating oil to depress the solidification temperature. The pour point depressant functions to inhibit formation of a three-dimensional network attributed to crystallization of the wax component in the lubricating oil and to depress the pour point of the lubricating oil.

20 [0004] Of the low-temperature properties of a lubricating oil containing a viscosity modifier having an effect of improving viscosity index and a pour point depressant, the viscosity at a high shear rate is determined by compatibility of a lubricating oil base with the viscosity modifier, but on the other hand, the viscosity at a low shear rate is greatly influenced by the pour point depressant. It is known that when an ethylene/ α -olefin copolymer having specific composition is used as a viscosity modifier, the effect of the pour point depressant is markedly reduced because of an interaction between the copolymer and the pour point depressant (see U.S. Patents No. 3,697,429 and No. 3,551,336).

25 [0005] Accordingly, the viscosity modifier to be blended with a lubricating oil which is required to have particularly excellent low-temperature properties is desired to exhibit an excellent effect of improving viscosity index and not to inhibit the function of the pour point depressant.

30 [0006] As a viscosity modifier satisfying such requirements, an ethylene/ α -olefin copolymer, which has an ununiform distribution of ethylene units and α -olefin units in the molecules, an ethylene content of 30 to 80 % by weight, a weight-average molecular weight of 20, 000 to 750, 000 and Mw/Mn of less than 2, is disclosed in Japanese Patent Publication No. 96624/1994.

35 [0007] The present inventors have earnestly studied under such circumstances as mentioned above, and as a result, they have found that an ethylene/propylene copolymer having a density, a molecular weight, a molecular weight distribution and a melting point in the specific ranges and having a specific relation between the density and the melting point and an ethylene/propylene copolymer having an ethylene content, a molecular weight, a molecular weight distribution and a melting point in the specific ranges and having a specific relation between the ethylene content and the melting point have an excellent effect of improving viscosity index and do not inhibit the function of the pour point depressant. Based on the finding, the present invention has been accomplished.

40 [0008] For reference, the ethylene/ α -olefin copolymer disclosed in the above publication satisfies neither the relation between the ethylene content and the melting point of the ethylene/propylene copolymer nor the relation between the density and the melting point of the ethylene/propylene copolymer specified by the present invention.

OBJECT OF THE INVENTION

45 [0009] It is an object of the present invention to provide a viscosity modifier for a lubricating oil, which comprises a specific ethylene/propylene copolymer and by which a lubricating oil composition having excellent low-temperature properties can be obtained, and to provide a lubricating oil composition containing the viscosity modifier and having excellent low-temperature properties.

DISCLOSURE OF THE INVENTION

50 [0010] One embodiment of the viscosity modifier for a lubricating oil according to the present invention comprises an ethylene/propylene copolymer (A) having the following properties (a-1) to (a-5):

(a-1) the density is in the range of 857 to 882 kg/m³,

(a-2) the weight-average molecular weight as measured by gel permeation chromatography is in the range of 80,000 to 400,000 in terms of polystyrene,

(a-3) Mw/Mn (Mw: weight-average molecular weight, Mn: number-average molecular weight), which is an indication of a molecular weight distribution, is not more than 2.3.

(a-4) the melting point as measured by a differential scanning calorimeter is in the range of 15 to 60°C, and

(a-5) the density (D (kg/m³)) and the melting point (Tm (°C)) as measured by a differential scanning calorimeter satisfy the following relation (I)

$$T_m \leq 1.247 \times D - 1037 \quad (I).$$

Another embodiment of the viscosity modifier for a lubricating oil according to the present invention comprises an ethylene/propylene copolymer (B) having the following properties (b-1) to (b-5):

(b-1) the content of recurring units derived from ethylene is in the range of 70 to 79 % by weight,

(b-2) the weight-average molecular weight as measured by gel permeation chromatography is not less than 80,000 and less than 250,000 in terms of polystyrene,

(b-3) Mw/Mn (Mw: weight-average molecular weight, Mn: number-average molecular weight), which is an indication of a molecular weight distribution, is not more than 2.3,

(b-4) the melting point as measured by a differential scanning calorimeter is in the range of 15 to 60°C, and

(b-5) the content (E (% by weight)) of recurring units derived from ethylene and the melting point (Tm (°C)) as measured by a differential scanning calorimeter satisfy the following relation (II)

$$3.44 \times E - 206 \geq T_m \quad (II).$$

A further embodiment of the viscosity modifier for a lubricating oil according to the present invention comprises an ethylene/propylene copolymer (C) having the following properties (c-1) to (c-5):

(c-1) the content of recurring units derived from ethylene is in the range of 70 to 79 % by weight,

(c-2) the weight-average molecular weight as measured by gel permeation chromatography is in the range of 250,000 to 400,000 in terms of polystyrene,

(c-3) Mw/Mn (Mw: weight-average molecular weight, Mn: number-average molecular weight), which is an indication of a molecular weight distribution, is not more than 2.3,

(c-4) the melting point as measured by a differential scanning calorimeter is in the range of 15 to 60°C, and

(c-5) the content (E (% by weight)) of recurring units derived from ethylene and the melting point (Tm (°C)) as measured by a differential scanning calorimeter satisfy the following relation (III)

$$3.44 \times E - 204 \geq T_m \quad (III).$$

[0011] When the viscosity modifier for a lubricating oil according to the present invention is blended with a lubricating oil, a lubricating oil having excellent low-temperature properties can be obtained.

[0012] Embodiments of the lubricating oil composition according to the present invention include:
a lubricating oil composition comprising

(A) the ethylene/propylene copolymer having the above properties (a-1) to (a-5), and

(D) a lubricating oil base,

wherein the ethylene/propylene copolymer (A) is contained in an amount of 1 to 20 % by weight;

a lubricating oil composition comprising

(B) the ethylene/propylene copolymer having the above properties (b-1) to (b-5), and

(D) a lubricating oil base,

wherein the ethylene/propylene copolymer (B) is contained in an amount of 1 to 20 % by weight; and a lubricating oil composition comprising

(C) an ethylene/propylene copolymer having the above properties (c-1) to (c-5), and

(D) a lubricating oil base,

wherein the ethylene/propylene copolymer (C) is contained in an amount of 1 to 20 % by weight.

[0013] Other embodiments of the lubricating oil composition according to the present invention include:

a lubricating oil composition comprising

- (A) the ethylene/propylene copolymer having the above properties (a-1) to (a-5),
- (D) a lubricating oil base, and
- (E) a pour point depressant,

wherein the ethylene/propylene copolymer (A) is contained in an amount of 0.1 to 5 % by weight and the pour point depressant (E) is contained in an amount of 0.05 to 5 % by weight:

a lubricating oil composition comprising

- (B) the ethylene/propylene copolymer having the above properties (b-1) to (b-5),
- (D) a lubricating oil base, and
- (E) a pour point depressant,

wherein the ethylene/propylene copolymer (B) is contained in an amount of 0.1 to 5 % by weight and the pour point depressant (E) is contained in an amount of 0.05 to 5 % by weight; and

a lubricating oil composition comprising

- (C) an ethylene/propylene copolymer having the above properties (c-1) to (c-5),
- (D) a lubricating oil base, and
- (E) a pour point depressant,

wherein the ethylene/propylene copolymer (C) is contained in an amount of 0.1 to 5 % by weight and the pour point depressant (E) is contained in an amount of 0.05 to 5 % by weight.

[0014] The lubricating oil composition according to the present invention has excellent low-temperature properties.

BEST MODE FOR CARRYING OUT THE INVENTION

[0015] The viscosity modifier for a lubricating oil and the lubricating oil composition according to the invention are described in more detail hereinafter.

Viscosity modifier for lubricating oil

[0016] An embodiment of the viscosity modifier for a lubricating oil according to the invention comprises the following ethylene/propylene copolymer (A).

Ethylene/propylene copolymer (A)

[0017] The ethylene/propylene copolymer (A) comprises recurring units derived from ethylene and recurring units derived from propylene. Although the ethylene content in the ethylene/propylene copolymer (A) is not specifically limited as far as the density is within such range as mentioned later, it is in the range of usually 70 to 79 % by weight, preferably 71 to 78 % by weight, more preferably 72 to 78 % by weight, still more preferably 73 to 77 % by weight, particularly preferably 75 to 77 % by weight. The residue is a content of recurring units derived from propylene and the like.

[0018] In the present invention, the ethylene content in the ethylene/propylene copolymer is determined by ¹³C-NMR in accordance with the method described in "Macromolecule Analysis Handbook" (Society of Japan Analytical Chemistry, edited by Macromolecule Analytical Research Meeting, published by Kinokuniya Shoten).

[0019] In the ethylene/propylene copolymer (A), recurring units derived from at least one monomer selected from α -olefins of 4 to 20 carbon atoms, cycloolefins, polyenes and aromatic olefins (hereinafter sometimes referred to as "other monomers") may be contained in amounts of, for example, not more than 5 % by weight, preferably not more than 1 % by weight, within limits not detrimental to the objects of the invention.

[0020] The ethylene/propylene copolymer (A) has a density of 857 to 882 kg/m³, preferably 859 to 880 kg/m³, more preferably 860 to 880 kg/m³, still more preferably 864 to 875 kg/m³, particularly preferably 868 to 875 kg/m³.

[0021] When the density is not less than 857 kg/m³, satisfactory low-temperature properties can be obtained. When the density is not more than 882 kg/m³, there is no fear that a lubricating oil composition is partially jellied at low temperatures owing to crystallization of an ethylene sequence portion in the ethylene/propylene copolymer.

[0022] The density is measured in accordance with ASTM D1505-85.

[0023] The molecular weight of the ethylene/propylene copolymer (A), as measured by gel permeation chromatography, is in the range of 80,000 to 400,000, preferably 100,000 to 380,000, particularly preferably 120,000 to 350,000,